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ON THE INFRARED SPECTRA OF p-FLUORO- AND o-, m-, AND p-CHLORO TOLUENE IN THE VAPOUR STATE

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ABSTRACT. The infrared spectra of each of parafluoro-, and ortho-, meta- and para-chlorotoluene in the vapour and liquid states and in solution have been recorded on the same chart in order to find any changes which may take place in the spectra with the change of phase. It has been observed that some of the bands given by the compounds in the vapour state excepting orthochlorotoluene are absent in the spectra due to the compounds in the liquid state. It has been concluded that formation of dimers in some percentages of the molecules takes place even in the vapour phase of these three compounds. Orthochloro toluene does not show such changes.

From a comparison of the infrared frequencies with the Raman frequencies of the compounds in the liquid state assignments of the frequencies have been made. It has been pointed out that some of the assignments made by previous workers need revision in view of the fact that the observed infrared bands cannot be explained satisfactorily by the earlier assignments.

INTRODUCTION

The infrared spectra of a very large number of mono- and disubstituted benzenes were investigated previously by many workers who used mostly solutions of the compounds in suitable solvents. Recently, the present authors pointed out (Sirkar *et al.*, 1964) that the spectra of fluoro-, chloro-, bromo- and iodobenzene in the vapur state show additional bands which are absent in the spectra of the compounds in the liquid state. It was concluded from a comparison of the spectra of each of these compounds in the two states that partial intermolecular association takes place in all these compounds even in the vapour state and the percentage of the associated molecules increases when the vapours are liquefied. A comparison of these spectra with the Raman spectra of the substances in the liquid state was found to be helpful in assigning the frequencies to different modes of vibration of the molecules.

Disubstituted benzenes in which one of the substituents is a halogen atom are expected to exhibit such association in the liquid state. The spectra of chlorotoluenes in the vapour state were not studied by any previous worker and although those of fluorotoluenes were studied both in liquid and vapour states by Thompson and Temple (1948) the significance of the changes in the spectra produced by the

change of the state was not discussed by those authors. Hence, the present investigation on the infrared spectra of parafluorotoluene, parachlorotoluene, orthochlorotoluene and metachlorotoluene in the vapour and liquid states and in solution in carbon tetrachloride and cyclohexane was undertaken with a view to finding out whether the spectra reveal the evidence of intermolecular association and also assigning the frequencies to different modes of vibration from a comparison of the spectra with the Raman spectra of the substances in the liquid state.

EXPERIMENTAL

The liquids supplied by British Drug House and Light and Company of England were of chemically pure quality and they were redistilled under reduced pressure. The purity of the liquids was tested by studying the Raman spectra.

The infrared spectra were recorded with a Perkin-Elmer model 21 double beam infrared spectrophotometer provided with NaCl prism. In the case of the pure liquid a thin film enclosed between two NaCl plates was used. A multiple reflection 100-cm gas cell supplied by Perkin-Elmer Corporation was used to record the infrared absorption spectra of the vapours at the room temperature. In the case of the solution, a compensation cell was placed in the reference beam, but the bands appearing in the positions of the strong bands of the solvents were suppressed. The spectrophotometer was calibrated with the help of the spectrum due to a thin sheet of polystyrene and the corrections required in observed frequencies in the different regions were found out and applied to get the correct values of the frequencies In order to find out the changes in the spectrum with the change from the vapour to the liquid phase, the spectra due to the two phases of each of the compounds were recorded on the same chart.

RESULTS AND DISCUSSIONS

The spectra are reproduced in Figs. 1, 2, 3 and 4 respectively. The corrected values of the observed frequencies are given in Tables I, II, III and IV in which, besides the bands due to the solutions, the Raman frequencies of the liquids reported by previous workers have also been included for comparison. The assignments of the frequencies in terms of the corresponding modes of benzene have been given in the last column of the Tables. The results are discussed separately in the following sections.

PARAFLUOROTOLUENE

The Raman frequencies of this liquid are taken from Mecke-Kerkhof (1951), but the three frequencies 311, 501 and 728 cm^{-1} are taken from Magat (1936).

It can be seen from Fig. 1 as well as Table I that the structure of some of the bands in the spectrum of the vapour changes when the vapour is liquefied. In he spectrum due to the vapour there are doublets at 720, 730 cm^{-1};

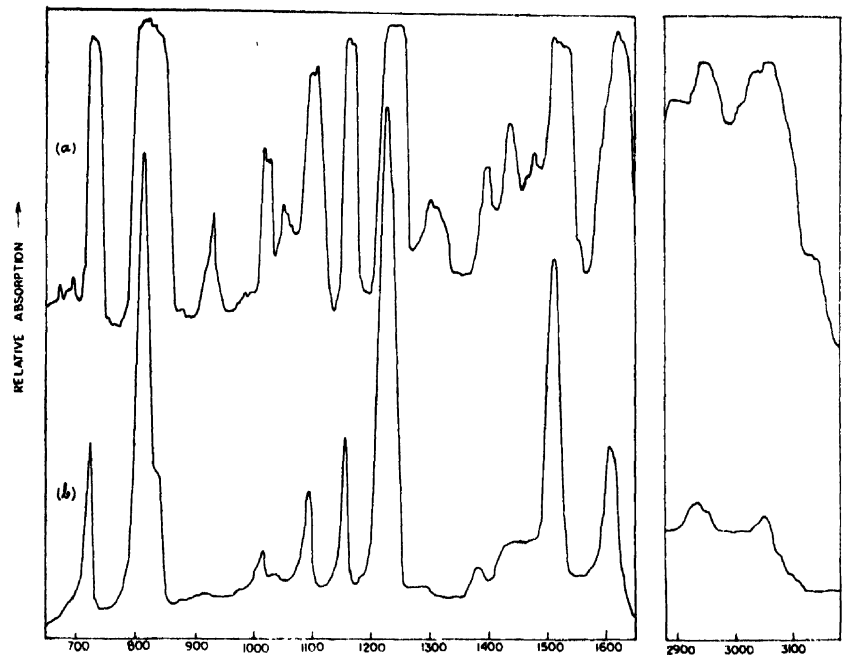

Fig. 1. Spectra of parafluorotoluene
(a) Vapour (b) Liquid

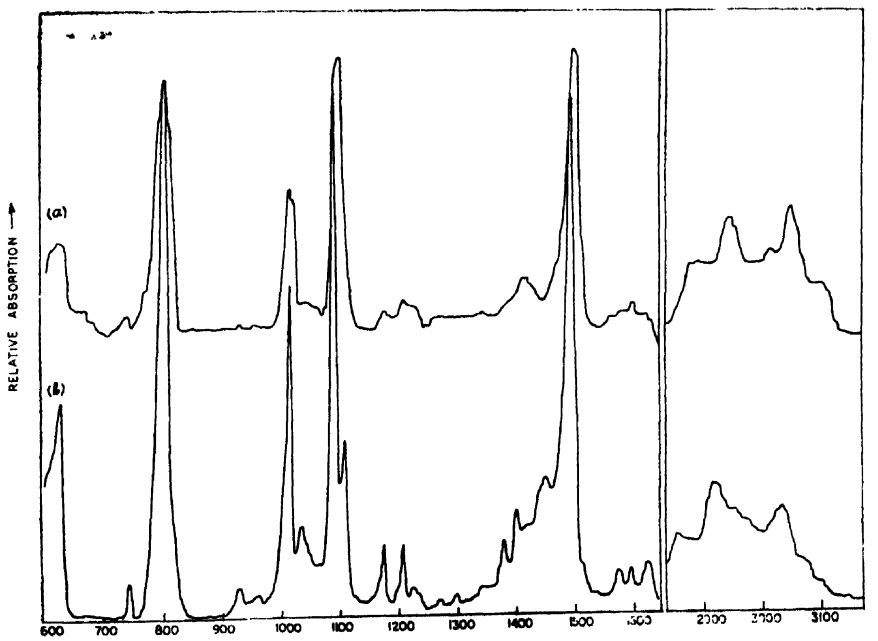

Fig. 2. Spectra of parachlorotoluene
(a) Vapour (b) Liquid

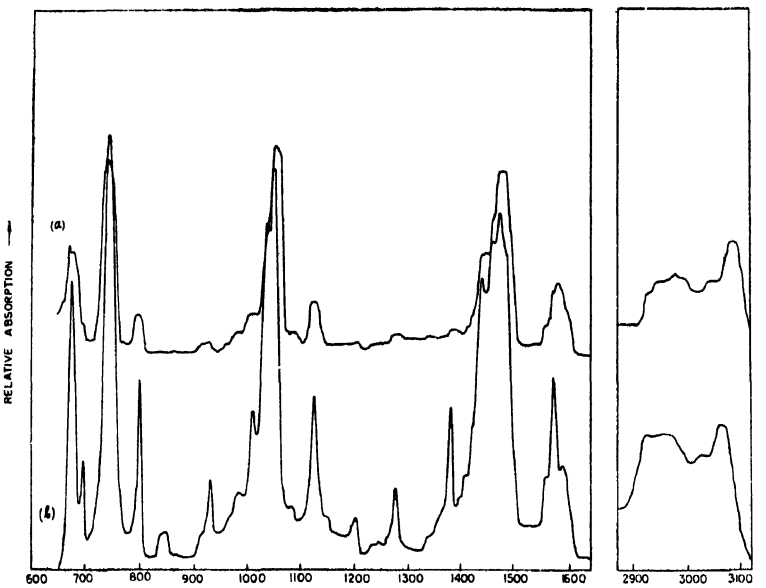

Fig. 3. Spectra of orthochlorotoluene
(a) Vapour (b) Liquid

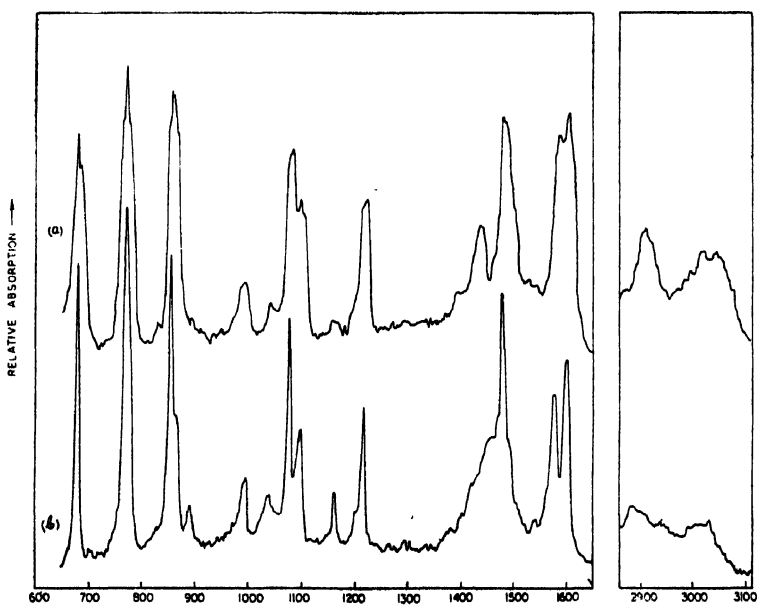

Fig. 4. Spectra of metachlorotoluene
(a) Vapour (b) Liquid

810, 820 cm^{-1}; 830, 840 cm^{-1}; 1095, 1104 cm^{-1}; 1158, 1166 cm^{-1} and 1232, 1248 cm^{-1} respectively, but in the corresponding positions the spectrum due to the liquid shows only single bands at 720, 810, 833, 1095, 1158 and 1222 cm^{-1} respectively. vidently, the vapour consists of two types of molecules. These are probably the single molecules and dimers formed by intermolecular hydrogen-bonding and the higher of the two frequencies in each doublet is the frequency of the single molecule. The frequencies reported by Thompson and Temple (1948) for the liquid differ slightly from those given in Table I. A comparison of the spectra due to the vapour and the liquid reproduced in Fig. 1, however, shows that the band of higher frequency in each of the doublets mentioned above is absent in the spectrum due to the liquid and this conclusion is not affected by any small error in calibration of the spectrophotometer which is less than 2 cm^{-1} in the region 610 -1200 cm^{-1}.

TABLE I

Parafluorotoluene

Raman frequencies (liquid) $\Delta\nu$ in cm^{-1}	Infrared frequencies in cm^{-1}				Assignment (corresponding modes of C_6H_6)
	Vapour	Liquid	Soln. in CCl_4	Soln. in cyclohexane	
311 (0)*					11
338 (3), *dp*					1C B
453 (3), *p*					6 A
501 (0.5)*					18 B
636 (2), *dp*					6 B
693 (0), *p*					3 (?)
				715 (10)	
	720 (s)	720 (s)			
728 (1)*	730 (s)			730 (m)	9 B
			805 (m)		
	810 (s)	810 (vs)			
			815 (vs)	817 (vs)	12
	820 (s)				
824 (6n), *p*					
	830 (s)				10 A
		833 (m)			
			838 (m)	838 (m)	
	840 (w)				
841 (3), *p*					
	847 (w)				1
	928 (m)				18 A
					17 A
1001 (0), *p*	1015 (m)	1015 (vw)		1015 (w)	
	1025 (m)				
				1030 (w)	
	1032 (w)				
			1090 (vw)		
	1095 (s)	1095 (m)			
			1098 (w)		19 A
	1104 (s)				
1157 (1), *p*	1158 (s)	1158 (m)	1160 (m)		9 A
	1166 (s)				

TABLE I (*contd.*)

Raman frequencies (liquid) $\Delta\nu$ in cm^{-1}	Infrared frequencies in cm^{-1}				Assignment (corresponding modes of C_6H_6)
	Vapour	Liquid	Soln. in CCl_4	Soln. in cyclohexane	
1211 (3b), *p*			1210 (vw)		2
				1216 (vw)	
	1222 (vw)	1222 (vs)			
	1232 (vs)		1230 (vs)	1232 (vs)	
	1248 (vs)				20 A
1297 (0), *p*	1292 (w)	1290 (vw)			13
	1378 (vw)	1378 (w)			CH_3 bending
1383 (1), *p*					
	1390 (m)				
	1415 (vvw)	1415 (w)			
	1429 (m)				
1453 (0), *dp*					
	1468 (vw)				CH_3 bending
	1505 (vs)	1505 (vs)	1505 (vs)		
	1516 (s)			1516 (s)	19 B
	1528 (s)				
	1584 (w)	1586 (w)			
1599 (1)	1598 (m)	1600 (m)	1602 (m)	1595 (vvw)	8 A
	1612 (vs)	1608 (m)	1610 (w)	1610 (w,b)	8 B
1615 (1)					
	1622 (s)				
	1632 (m)				
	1735 (w)				
	1742 (w)				
	1752 (m)				
	1870 (m)	1865 (m)	1865 (vw)		
	1880 (m)	1875 (m)	1875 (vw)		
	1978 (w)				
	2085 (vw)				
	2400 (vw)				
	2465 (vw)				
2739 (0)					
	2750 (vw)				
	2850 (vw)	2850 (m)			
2872 (3)		2885 (m)			
	2890 (m)				
	2900 (s)	2900 (m)			
2926 (3)	2930 (vw)	2930 (s)			CH_3 valence
	2940 (vs)				
		2950 (w)			
	2960 (vs)				
	3020 (s)				
	3030 (s)	3030 (s)	3030 (m)	3030 (m)	
	3040 (s)	3040 (vw)			
3048 (7)					7 B
3073 (9)	3075 (m)	3075 (w)	3070 (vw)	3070 (vw)	20 B & 2′
	3115 (m)				
3207 (0)					

The frequency 841 cm^{-1} has been assigned to a mode corresponding to the breathing vibration of benzene. This frequency has been assigned by Mecke-Kerkhof (1951) to C-F valence oscillations, but the fact that the corresponding infrared band is extremely weak shows that such an assignment is not correct. The frequency of the mode in the single molecule is 847 cm^{-1} as shown by the weak infrared band. The assignment of the frequency 1095 cm^{-1} of the liquid to mode No. 19A (Pitzer and Scott, 1943) is in accordance with such an assignment made in the case of similar molecules by Mecke-Kerkhof (1951). The Raman line 1211 cm^{-1} of the liquid is highly polarized, but this frequency is absent in the infrared spectrum of the liquid. So the mode of this frequency is of symmetric type and cannot be assigned to ν_{12} as has been done by Mecke-Kenkhof (1951). Hence this frequency has been assigned to a mode similar to mode No. 2 of benzene in which the C-F, C-CH_3 and C-H valence oscillations take part simultaneously in phase with each other. Similarly, the frequency 1248 cm^{-1} has been assigned to a mode of the single molecule arising from ν_{20A} of benzene and the corresponding frequency in the dimer is 1222 cm^{-1}. Again, the frequency 1297 cm^{-1} has been assigned to a mode similar to ν_{13} of benzene and not to ν_{19A}. The frequency 1608 cm^{-1} of the liquid which is assigned to mode ν_{8B} of benzene ring has two more companions at 1622 and 1632 cm^{-1} respectively in the case of the vapour. The frequency 1622 cm^{-1} may be that of the single molecule and 1632 cm^{-1} may be due to an alternative configuration of the mode as suggested previously (Sirkar *et al.*, 1964) in the case of mono substituted benzenes. The frequency 1600 cm^{-1} is assigned to ν_{8A} of the ring, as done by the above authors.

As regards the frequencies of C-H valence oscillations it appears that the strong 3030 cm^{-1} band of the liquid is due to a mode different from that producing the strong Raman line 3048 cm^{-1}. This line is evidently due to a mode similar to ν_{7B} of benzene which is forbidden in the infrared spectrum. The band 3030 cm^{-1} may then be due to ν_{20B} of benzene in the dimer formed by association, the band 3075 cm^{-1} due to the vapour being the corresponding band of the single molecule. The strong Raman line 3073 cm^{-1} is also produced by a mode different from ν_{20} which is forbidden in the Raman effect and it appears that when hydrogen-bonding takes place between the hydrogen atoms of the CH_3 group and the fluorine atom, as indicated by the change in the relative intensities of the bands 2940 and 2930 cm^{-1} with the change of state, the C-H vibrations in the four C-H groups of the ring take place in accordance with the symmetry of ν_2 of benzene and such a mode produces the Raman line 3073 cm^{-1}.

It is therefore concluded that the vapour of parafluorotoluene is a mixture of single molecules and dimers while the liquid consists almost wholly of dimers.

PARACHLOROTOLUENE

In the case of parachlorotoluene also there is a strong polarised Raman line at 796 cm^{-1}, but the corresponding infrared band is weak, This frequency has

TABLE II

Parachlorotoluene

Raman frequencies (liquid) $\Delta\nu$ in cm^{-1}	Infra red frequencies in cm^{-1}				Assignment (corresponding modes of C_6H_6)
	Vapour	Liquid	Soln. in CCl_4	Soln. in cyclohexane	
304 (3), *dp*					10 B
377 (12), *p*					6 A
	612 (vw)	610 (w)			
	624 (m)	626 (s)			18 A
635 (3), *dp*	634 (w)		630 (s)		
	638 (w)				6 B
				672 (vw)	
692 (0), *dp*					9 B
	720 (vvw)				
	742 (w)	742 (w)			
796 (5), *p*	795 (m)				1
	805 (s)	802 (vs)		802 (s)	12
	810 (m)				10'A
819 (1), *p*					
	1012 (s)	1013 (vs)			
	1020 (m)				17 A
1036 (1)	1030 (vw)	1030 (w)			
	1045 (w)	1045 (vw)			
1090 (5), *p*	1088 (m)	1088 (vs)			
	1096 (vs)				19 A
	1106 (vw)	1106 (w)	1106 (s)		
1175 (1)	1172 (vw)	1172 (w)	1172 (m)	1172 (w)	9 A
1208 (3), *p*	1208 (w)	1208 (w)	1206 (w)	1208 (w)	2
	1225 (vw)		1225 (vvw)		
			1296 (vw)		7 A (?)
1303 (0)					13 (?)
1377 (2), *p*		1375 (w)	1380 (m)		CH_3 bending
	1392 (vvw)				
		1396 (w)			
			1402 (s)		
	1408 (w)				
			1418 (vw)		
	1442 (vw)	1445 (vw)			
1452 (0), *dp*	1455 (w)		1450 (s)		CH_3 bending
			1475 (vs)		
	1490 (s)	1490 (vs)			19 B
	1498 (s)				
	1570 (vvw)	1572 (w)		1575 (w)	
1596 (8), *p*	1596 (w)	1592 (w)		1598 (w)	8 A
	1618 (vvw)	1620 (w)		1624 (s)	8 B
	1628 (vw)		1630 (s)		

TABLE II (*contd.*)

Raman frequencies (liquid) $\Delta\nu$ in cm^{-1}	Infra red frequencies in cm^{-1}				Assignment (corresponding modes of C_6H_6
	Vapour	Liquid	Soln. in CCl_4	Soln. in cyclohexane	
			1720 (w)	1720 (w)	
			1772 (m)	1770 (vw)	
	1880 (w)	1880 (m)	1890 (s)	1885 (s)	
	1890 (w)				
		2855 (m)			
	2885 (m)		2880 (s)		
	2920 (vw)	2920 (vs)			
2922 (3), *p*			2930 (vs)		CH_3 valence
	2940 (vs)				
		2950 (vw)			
			2970 (w)		
	2985 (w)				
			2990 (w)		
	3010 (vw)	3010 (vw)			
	3035 (vs)	3020 (s)	3026 (vs)		
3047 (2)					
3062 (4)		3060 (m)			7 B
3070 (1)	3080 (m)		3070 (m)		2′
					20 B

been assigned to the total symmetric vibration similar to ν_1 of benzene and not to C-Cl valence oscillation alone. The bands 805, 1012, 1030, 1088, 1208, 1490 and 2920 cm^{-1} have close companions at 810, 1020, 1045, 1096, 1225, 1498 and 2940 cm^{-1} respectively in the spectrum due to the vapour, but these latter bands are absent in the spectrum due to the liquid. Hence in this case also the vapour consists of monomeric and dimeric molecules, the percentage of the latter being smaller than that in the case of parafluorotoluene in the vapour state. The liquid seems to consist wholly of associated molecules. As in the case of parafluorotoluene the mode ν_{12} has the frequency 810 cm^{-1} in the single molecule and 802 cm^{-1} in the associated molecules in the liquid, this frequency being much lower than 1208 cm^{-1} assigned by Mecke-Kerkhof (1951) to this mode. There is no reason why the frequency of this mode in this substituted molecule should be higher than that in benzene. The fact that this frequency does not appear in the Raman spectrum of the liquid clearly indicates the correctness of its assignment to a mode of the ring which is of symmetry b_{1u}. In this case also the mode giving the strong and polarized Raman line 1208 cm^{-1} produces only a weak band in the infrared, and therefore, this frequency has been assigned to a mode similar to ν_2 of benzene. The assignment of the frequency 1096 cm^{-1} to ν_{19A} of the ring of the monomeric molecule agrees with that of the frequency 1090 cm^{-1} made by Mecke-Kerkhof (1951) to this mode in the liquid. In this case also the change in the CH_3 frequencies with the change of phase indicates the formation of

hydrogen bonds in the liquid. The Raman lines 3047 and 3062 cm^{-1} are to be assigned respectively to ν_{7B} and ν_2 of the dimers as in the case of parafluorotoluene, while ν_{20B} has the value 3080 cm^{-1} in the case of the single molecule and 3020 cm^{-1} in the associated molecule in the liquid.

ORTHOCHLOROTOLUENE

The Raman frequencies of this liquid have been taken both from Magat (1936) and Mecke-Kerkhof (1951). A comparison of the infrared bands for the vapour and the liquid shows that except the bands at 1060 cm^{-1} and 1580 cm^{-1} all the other bands of high and medium strengths given by the vapour appear also in the spectrum of the liquid. The two bands 668 and 676 cm^{-1} of the vapour are replaced by a single band of intermediate frequency 672 cm^{-1}. The band 743 cm^{-1} is also produced in the same way in place of the two sharp bands 740 and 745 cm^{-1}. Probably the intermolecular forces in the liquid make the components

TABLE III

Orthochlorotoluene

Raman frequencies (liquid) $\Delta\nu$ in cm^{-1}	Infra red frequencies in cm^{-1}				Assignment (corresponding modes of C_6H_6)
	Vapour	Liquid	Soln. in CCl_4	Soln. in cyclohexane	
166 (8), *dp*					10 B
247 (5), *dp*					10 A
361 (3), *dp*					6 A
447 (4)					18 B
552 (7)					6 B
	668 (m)				
		672 (s)			
678 (6), *p*	676 (m)		674 (vs)	676 (s)	9 B
	695 (vw)	695 (w)	694 (vw)	696 (m)	
745 (1)	740 (s)	743 (s)		740 (vs)	12
	745 (m)				
	795 (vw)				
803 (4)	800 (vw)	800 (m)		802 (m)	1
		847 (vw)			
852 (00)					
				910 (vvw)	
	918 (vvw)	918 (vvw)			
	930 (vvw)	930 (m)	933 (m)	932 (w)	
989 (1)	985 (vvw)	986 (m)	986 (w)	986 (w)	17 A
1016 (0)	1012 (vw,b)	1012 (m)	1012 (w)	1010 (s)	
	1038 (m)	1036 (s)	1038 (vs)	1025 (m)	
1045 (8), *p*				1040 (m)	
	1050 (vs)	1050 (vs)	1050 (s)	1050 (s)	19 A
	1060 (s)				

TABLE III—(*contd*).

Raman frequencies (liquid) $\Delta\nu$ in cm^{-1}	Infra red frequencies in cm^{-1}				Assignment (corresponding modes of C_6H_6)
	Vapour	Liquid	Soln. in CCl_4	Soln. in cyclohexane	
			1086 (vw)	1086 (vw)	
	1124 (vw)	1124 (m)	1126 (s)	1127 (m)	
1132 (2)					
1156 (2)			1152 (vw)		9 A
1204 (5)	1204 (vvw)	1206 (w)	1203 (vvw)	1206 (vw)	2
1279 (0.5)	1278 (w,b)	1273 (w)	1278 (m)		7 A
				1342 (vvw)	
	1380 (vw)	1380 (m)	1382 (s)	1374 (vw)	CH_3 bending
			1408 (vw)		
1426 (0)	1422 (vvw)		1425 (w)		CH_3 bending
	1442 (m)	1440 (m)	1442 (vs)		
	1460 (w)	1460 (m)	1460 (m)		
	1472 (vs)	1472 (vs)	1470 (s)		
	1482 (vs)	1482 (w)			
	1560 (vw)	1560 (vw)			19 B
1574 (3)	1570 (vw)	1570 (m)		1573 (m)	8 A
	1580 (m)				
1592 (3)	1590 (vw)	1590 (w)		1594 (m)	8 B
	1600 (vw)				
			1670 (w)	1670 (vvw)	
	1780 (vw,b)		1785 (m)	1780 (w)	
	1820 (vvw)		1830 (w)	1820 (vw)	
			1870 (vw)	1865 (vvw)	
	1905 (vw)		1908 (m)	1904 (w)	
	1950 (vw)		1950 (m)	1950 (w)	
2859 (0)	2850 (vw)	2855 (vw)			
			2870 (m)		
	2880 (w)	2880 (w)			
2926 (5)	2930 (m)	2930 (s)		2930 (m)	CH_3 valence symmetric
			2940 (s)		
	2950 (s)	2950 (s)			
			2960 (s)	2960 (m)	
	2970 (s)	2970 (s)			
			2980 (m)	2980 (m)	CH_3 valence asymmetric
					7 B
3013 (0)					
		3025 (w)	3020 (w)	3020 (vw)	
	3040 (w)				
		3055 (s)	3055 (vs)	3055 (vs)	20 B
					2′
3062 (7)					
	3080 (s)				

of the bands too broad to be resolved. The disappearance of the bands 1060 cm^{-1} and 1580 cm^{-1} is, however, of different nature. It seems that each of these modes

has two alternative configurations in the vapour but one of these cannot take place in the liquid So, it is concluded that the vapour consists of single molecules and in the liquid also the intermolecular forces are too weak to change the frequencies appreciably. The frequencies of CH_3 valence oscillations also remain unchanged with the change of state, which shows that no hydrogen bond is formed in this case through the CH_3 group.

In assigning the Raman frequencies in the region 100 cm^{-1} to 600 cm^{-1} the expected change of frequency of vibration with substitution has been chosen as the guiding factor. The two lines 247 cm^{-1} and 166 cm^{-1} are depolarised and very intense. So, they have been assigned to modes similar to ν_{10A} and ν_{10B} of benzene in which the displacements are perpendicular to the plane of symmetry. Similarly, the lines 552 cm^{-1} and 361 cm^{-1} have been assigned respectively to modes similar to ν_{6B} and ν_{6A} of benzene, because the frequency of the former mode should be larger than that of the latter mode. The line 447 cm^{-1} is evidently due to an in-plane vibration and has been assigned to ν_{18B}. In place of the strong and polarised Raman line 678 cm^{-1} there is a strong infra-red band. So the corresponding mode is derived from a centro-symmetric mode of benzene and ν_{9B} has been chosen for this frequency. In ν_{9A} either the chlorine atom or the CH_3 group may remain at rest and this may give rise to two different frequencies. The Raman lines 1156 cm^{-1} and 1132 cm^{-1} have been assigned to these two alternative configurations. In the spectrum of the liquid there is a strong Raman line 1045 cm^{-1} and a strong infrared band at 1050 cm^{-1}. This is assigned to a mode similar to ν_{19A} of benzene. As in the previous two cases, the strong Raman line 1204 cm^{-1} is due to a mode derived from a symmetric mode of benzene and therefore it has been assigned to ν_2.

It is found that the frequencies of the bands due to CH_3 valence oscillation remain unchanged with the change from vapour to the liquid phase, but the bands 3080 cm^{-1} and 3040 cm^{-1} due to C-H valence oscillation of the benzene ring shift respectively to 3055 cm^{-1} and 3025 cm^{-1} with liquefaction of the vapour. These two bands can be assigned to modes similar to ν_{20B} and ν_{7B} of benzene respectively and it seems that such oscillations can take place even when one of the four C-H groups is substituted by a CX group. The shift may be due to influence of dielectric constant of the liquid, because even in the solutions such a shift takes place. The Raman line 3062 cm^{-1} is also due to a vibration in which symmetric C-H valence oscillation takes place in two diametrically opposite C-H groups.

METACHLOROTOLUENE

The Raman frequencies of the liquid included in Table IV are taken from the data reported by Biswas (1955). A comparison of the infrared bands due to the vapour with those due to the liquid shows that the bands at 774, 854, 859, 1082, 1100, 1482 and 3080 cm^{-1} produced by the vapour are absent in the spectrum

TABLE IV

Metachlorotoluene

Raman frequencies (liquid) $\Delta\nu$ in cm^{-1}	Infrared frequencies in cm^{-1}				Assignment (corresponding modes of C_6H_6)
	Vapour	Liquid	Soln in CCl_4	Soln in cyclohexane	
187 (5), *dp*					10 B
222 (5), *dp*					10 A′
247 (5), *dp*					10 A
394 (1), *p*					18 B
419 (7), *p*					6 A
522 (6), *p*					6 B
	670 (w)				
	676 (s)	676 (vs)	676 (vs)		
683 (7), *p*	682 (m)			680 (vs)	
	687 (w)				9 B
				745 (vw)	
	758 (w)				
	763 (w)				
	768 (vs)	768 (vs)	770 (vs)	766 (vs)	
775 (2)	774 (m)			772 (w)	12
				776 (m)	
	850 (m)	851 (vs)	850 (s)		
	854 (s)				
	859 (s)		859 (vw)		
861 (3), *p*					18 A
		863 (m)			
	864 (m)				
884 (0)					
		890 (vw)	890 (s)		
948 (0)					
			983 (m)	988 (s)	
	990 (w)	992 (w)			
998 (10), *p*					1
1042 (1)	1036 (vw)	1036 (vw)	1036 (s)		
	1075 (s)	1074 (s)	1072 (vs)	1074 (vs)	
1077 (4), *p*					
	1082 (m)			1080 (m)	19 A
1102 (2)	1095 (m)	1095 (m)	1094 (vs)	1095 (w)	9 A′
	1100 (w)				
1160 (2)	1160 (vvw)	1160 (w)	1162 (s)	1162 (s)	9 A
			1200 (m)		
				1206 (m)	
1209 (1)	1210 (m)		1210 (m)		7 A
1219 (4), *p*	1215 (w)	1215 (m)		1215 (vs)	2
			1292 (vw)		
			1330 (vvw)		
			1378 (vw)		

TABLE IV—(*contd*).

Raman frequencies (liquid) $\Delta\nu$ in cm^{-1}	Infrared frequencies in cm^{-1}				Assignment (corresponding modes of C_6H_6)
	Vapour	Liquid	Soln. in CCl_4	Soln. in cyclohexane	
1383 (2), *p*	1385 (vvw)		1385 (vw)		CH_3 bending
			1400 (m)		
	1430 (m)		1420 (m)		
	1450 (vw)	1450 (w)	1450 (vs)		
	1465 (w)	1462 (vw)	1462 (w)		
	1475 (s)	1473 (vs)	1475 (s)		19 B
	1482 (m)				
	1490 (vw)	1490 (vw)	1492 (vw)		
	1570 (w)	1570 (m)	1570 (m)		
1574 (3), *dp*	1575 (w)				
	1582 (m)			1580 (s)	8 A
		1592 (s)	1592 (vs)		
	1598 (vs)			1598 (m)	
1601 (4), *dp*	1607 (w)			1606 (s)	8 B
			1940 (m)	1940 (m)	
		2840 (vw)			
2862 (2)	2860 (w)		2865 (m)		
	2905 (vw)	2902 (m)			
2962 (6b), *p*	2925 (s)	2925 (vw)	2930 (vs)		CH_3 valence
	2955 (vvw)	2950 (vw)	2955 (w)		
	3000 (vw)	3000 (w)	2980 (w)		
	3020 (m)	3020 (m)	3025 (s)		
	3050 (m)	3050 (vvw)	3050 (s)		
3062 (10b), *p*					2′ & 7 A′
	3080 (w)		3080 (w)		20 B

of the liquid. These are weaker companions of the adjacent strong bands. The disappearance of these weaker bands shows that probably they are due to the small percentage of the single molecules present in the vapour and that in the liquid almost all the molecules are dimers formed by intermolecular association.

The Raman lines 998, 1219 and 1209 cm^{-1} have been assigned respectively to modes similar to ν_1, ν_2 and ν_{7A} of benzene. The line 1077 cm^{-1} is represented by a strong band in the infrared spectrum and therefore it has been assigned to ν_{19A}. The assignment of this frequency agrees with that made by Mecke-Kerkhof (1951), but it disagrees with the assignment made by Katritzky and Simmons (1959) who assume the frequency of ν_{19A} in this case to be 1476 cm^{-1}. In the case of parachlorotoluene also they have made similar assumption. The Raman line 1102 cm^{-1} may be due to an alternative configuration of ν_{9A} in which the CH_3 group remains at rest.

The frequencies of CH_3 valence oscillations seem to remain unaltered with the change of phase in this case, but the relative intensities of some of the bands due

to CH_3 and C-H oscillations undergo remarkable changes. Thus, the bands 2925 cm^{-1} and 3050 cm^{-1} become very weak and the bands 2902 cm^{-1} and 3020 cm^{-1} become stronger when the vapour is liquefied. The frequency 3020 cm^{-1} may be that of the dimeric molecule in the liquid. The Raman line 3062 cm^{-1} is evidently due to a mode different from that producing the infrared band 3020 cm^{-1} and it may be due to symmetric valence oscillation in two dimetrically opposite C-H groups. Such an oscillation is possible both in ν_2 and ν_{7B} with the same frequency and therefore this Raman line has been assigned to two such modes designated as ν_2 and ν_{7B}.

As regards the Raman lines in the region 180-600 cm^{-1} it is significant that in place of the two depolarised lines 247 and 166 cm^{-1} due to orthochlorotoluene, three depolarised lines at 247, 222 and 187 cm^{-1} are given by metachlorotoluene. The frequency 247 cm^{-1} is assigned to a mode corresponding to ν_{10A} in which the chlorine atom remains at rest. When the CH_3 group remains at rest in a similar mode (marked 10A′ in Table IV) the frequency is lowered and the line 227 cm^{-1} may be due to such a mode. In the case of orthochlorotoluene also such an alternative mode would be expected, but probaly the two components produce a broad band and are not resolved from each other.

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